



PATENT SPECIFICATION

NO DRAWINGS

974 108

Date of Application and filing Complete Specification: Jan. 13, 1961.

No. 1600/61.

Application made in Germany (No. F30276 IVc/8m) on Jan. 13, 1960.

Complete Specification Published: Nov. 4, 1964.

© Crown Copyright 1964.

Index at acceptance:—D1 B(2A2, 2B1D, 2B1E, 2B2B, 2C1A4B, 2C1B2)

International Classification:—D 06 p

COMPLETE SPECIFICATION

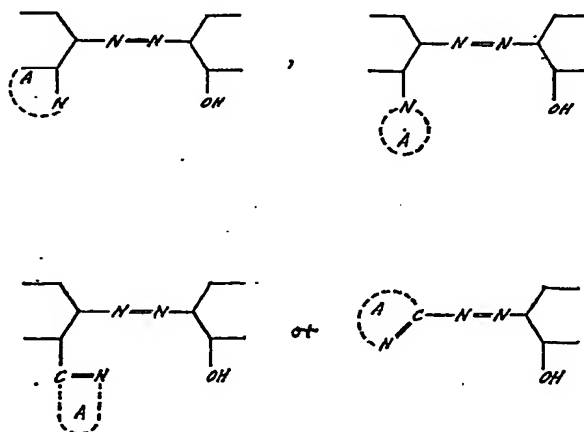
Process for the production of Dyeings or Prints of Metalliferous Azo-Dyestuffs on Textile Materials

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate recognised under German law, of 16 Frankfurt(M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides a process for the production of metalliferous water-insoluble azo-dyestuffs on textile fibrous materials.

U.S. Specification No. 2,768,053 describes a process for the production of metalliferous water-insoluble azo-dyestuffs on fibrous materials, wherein the fibrous material, dyed with a water-insoluble azo-dyestuff containing in ortho:ortho'-position to the azo-linkage groups capable of forming metal complexes, is after-treated in a bath having an alkaline reaction and containing a soap, a salt of hydroxide of copper, nickel or cobalt capable of forming complexes and an aliphatic amino- or hydroxy-carboxylic acid. In this process there are preferably used dyestuffs obtained by coupling a diazotized ortho-hydroxy- or ortho-methoxy-amine of the benzene series with a coupling component of the ice colour series, and which dyestuffs therefore contain an ortho:ortho'-dihydroxy- or ortho-hydroxy-ortho'-methoxy-azo-grouping. The dyeings so obtained possess better properties of fastness to light and chlorine than the non-metallized dyeings.

The present invention is based on the observation that valuable dyeings and prints of metalliferous water-insoluble azo-dyestuffs can be produced on textile fibrous materials by forming on the fibre a water-insoluble azo-dyestuff containing a grouping of the formula



in which A represents a 5- or 6-membered heterocyclic ring, and after-treating the dyed or printed material in an aqueous bath at a raised temperature with a salt of copper, nickel or cobalt, a compound capable of forming a metal complex with copper, cobalt or nickel and a detergent or a dispersing agent.

The azo-dyestuffs which are converted into complex metal compounds in the pro-

[Price 4s. 6d.]

cess of the invention, and containing a grouping of the above formulae are obtained by coupling on the fibre a diazonium compound of the corresponding heterocyclic amine with a coupling component which is free from groups imparting solubility in water, for example, sulphonic or carboxylic acid groups, and couples in a position vicinal to a hydroxyl group.

As such coupling components there are used, more especially, arylides of aromatic or heterocyclic ortho-hydroxy-carboxylic acids or of acylacetic acids, or other aromatic or heterocyclic hydroxy-compounds or compounds which contain an enolizable or enolized keto-methylene group in a heterocyclic ring. Such compounds are, for example, arylides of 2:3-hydroxy-naphthoic acid or substitution products thereof substituted in the 6-position, or arylides of 2-hydroxy-anthracene-3-carboxylic acid, of cresotinic acids, of halogen-salicylic acids, of 4-hydroxydiphenyl-3-carboxylic acid, of 2-hydroxy-carbazole-3-carboxylic acid, of 5-hydroxy-1:2;1':2'-benzocarbazole-4-carboxylic acid, of 3-hydroxy-diphenylene oxide-2-carboxylic acid, of 3-hydroxy-diphenylene sulphide-2-carboxylic acid, of acetoacetic acid, of benzoylacetic acid or of terephthaloyl-bis-acetic acid; hydroxybenzenes substituted in para-position, for example, 4-chloro-1-hydroxybenzene, 4-methyl-1-hydroxybenzene, 4-isopropyl-1-hydroxybenzene, 4-tert-butyl-1-hydroxybenzene, 4-acylamino-1-hydroxybenzene or 3-amino-4-methyl-1-hydroxybenzene; polyhydroxybenzenes, for example, 1:3-dihydroxybenzene, 1:3:5-trihydroxybenzene, 2:4-dihydroxybenzophenone or 1:4-di-(2':4'-dihydroxybenzoyl)-benzene; hydroxynaphthalenes, for example, 2-hydroxynaphthalene, 6-bromo-2-hydroxynaphthalene, 6-methoxy-2-hydroxynaphthalene, 7-methoxy-2-hydroxynaphthalene, 1-acylamino-7-hydroxynaphthalene, 5-chloro-1-hydroxynaphthalene, 4-chloro-1-hydroxynaphthalene, 5:8-dichloro-1-hydroxynaphthalene, 1-acylamino-7-hydroxynaphthalene, 7-benzoylamino-2-hydroxynaphthalene, 1-hydroxynaphthalene-5-sulphonic acid amide, 1-hydroxy-4-methoxynaphthalene, 1-hydroxy-4-benzoylnaphthalene, 2-hydroxynaphthalene-3-carboxylic acid methyl ester, 2-hydroxynaphthalene-6-carboxylic acid arylides, 2-hydroxynaphthalene-6-sulphonic acid amides or 2-hydroxynaphthalene-6-alkyl-sulphones; dihydroxynaphthalenes, for example, 1:3-, 2:6- or 2:7-dihydroxynaphthalene; pyrazolones, for example, 1-phenyl-5-pyrazolone-3-carboxylic acid amides, 1-phenyl-3-methyl-5-pyrazolone, 1-(4'-chlorophenyl)-3-methyl-5-pyrazolone, 1-(2':5'-dichlorophenyl)-3-methyl-pyrazolone or 1-(naphthyl-2')-3-methyl-5-pyrazolone; or derivatives of barbituric acid.

As heterocyclic amines there may be mentioned, for example, 2-(2'-aminoaryl)-4:5-arylene-1:2:3-triazoles, 2-(2'-aminoaryl)-4:5-arylene-1:2:3-triazole-1-oxides, 8-aminoquinoline, 7-aminoindazole, 3-aminoindazole, 7-aminobenzimidazole, 7-aminobenzotriazole, 1-aminocarbazole, 2-(2'-aminophenyl)-benzimidazole, 2-(2'-aminophenyl)-benzthiazole or derivatives thereof, 1-(2'-aminoaryl)-1:2:3:4-tetrazoles, 5-(2'-aminoaryl)-1:2:3:4-tetrazoles, 2-(2'-aminoaryl)-1:3:4-triazoles, 2-(2'-aminoaryl)-1:3:4-oxdiazoles, 2-(2'-aminoaryl)-1:3:4-thiodiazoles, 4-aminobenzo-2:1:3-thiadiazole or derivatives thereof and 3-amino-1-phenyl-5-imino-4:5-dihydro-1:2:4-triazole.

As fibrous materials there are used, more especially, cotton or regenerated cellulose, or also wool, silk, acetate rayon, polyamide or polyvinyl alcohol fibres.

The metallisation of the dyeings or printings, produced with the aforesaid diazo- and coupling components by methods in themselves known, is carried out at a raised temperature, preferably within the range of 80°C. to 100°C. in an aqueous alkaline bath, preferably in a bath rendered alkaline with sodium carbonate, the bath containing a salt of Cu, Ni or Co, compound capable of forming a complex therewith a dispersing agent or detergent, for example, a fatty alcohol polyglycol ether, an alkyl-phenol polyglycol ether, an alkyl-naphthol polyglycol ether, a fatty acid amide polyglycol ether, a fatty acid polyglycol ester, a condensation product of an aminoalkyl- or hydroxyalkyl-sulphonic acid and a fatty acid of high molecular weight, or an alkyl-aryl sulphonate.

Alternatively, the dyeing or print is first treated with a bath containing a dispersing agent or a detergent, a salt of copper, nickel or cobalt, a compound capable of forming a complex with Cu, Ni or Co and a compound capable of splitting off an alkali on heating, for example, the sodium salt of trichloroacetic acid, and subsequently steamed, during which the alkali is liberated and the metal complex is formed.

In other cases, it is not necessary to add an agent splitting off alkali, and the goods may be treated, before steaming, with a solution having an alkaline reaction and containing a dispersing agent or detergent, a salt of Cu, Ni or Co and a compound capable of forming a complex with Cu, Ni or Co.

As copper, nickel or cobalt salts there are preferably used the water-soluble salts of

said metals of an inorganic acid, such as the sulphates, chlorides, bromides, nitrates; of a low molecular aliphatic carboxylic acid, such as the acetates or formates; or of an organic sulphonic acid. Cobalt salts are advantageously used together with an oxidizing agent, for example, alkali metal perborate, persulphate or percarbonate.

As compounds capable of forming complexes with Cu, Ni or Co there may be mentioned, more especially, alkali metal phosphates such as alkali metal metaphosphates, alkali metal pyrophosphates or alkali metal polyphosphates; alkanolamines, such as diethanolamine or triethanolamine; aliphatic dicarboxylic acids such as oxalic acid or maleic acid; aliphatic hydroxycarboxylic acids, for example, citric acid, tartaric acid, lactic acid or gluconic acid; or aliphatic amino-carboxylic acids, for example aminoacetic acid, nitrilotriacetic acid, ethylene diamine tetracetic acid or glutamic acid, the choice of the compounds capable of forming complexes depending on the stability to alkali of the complex metal compound formed therewith.

The process of the invention is especially advantageous for the production of white or coloured discharges by first producing the white or coloured discharge on the unmetallised azoic dyeing in the usual manner, and then subjecting the material to the after-treatment of the invention. The process may also be carried out in that the non-metallized dyeings are treated with a salt of copper, nickel or cobalt, a compound capable of forming a complex therewith, a dispersing agent or detergent and an agent capable of splitting off an alkali, then printed with a discharge paste and finally steamed. In this manner purer discharges are obtained than by the usual metallisation followed by after-treatment with a detergent or dispersing agent.

In the process of the invention in which the treatment bath contains, in addition to a salt of Cu, Co or Ni and a compound capable of forming a complex with Cu, Co or Ni, a dispersing agent or detergent, the metal complexes are formed more rapidly and often at a lower temperature than in the process described in U.S. Specification No. 2,768,053.

The following Examples illustrate the invention:

EXAMPLE 1

A cotton fabric is dyed in a continuous manner on a foulard by grounding the fabric with a solution containing, per litre of water, 6.08 grams of 1-(2¹:3¹-hydroxynaphthoylamino)-2-methoxybenzene, drying the grounded fabric, and then passing it through a diazo solution containing, per litre of water, 5.4 grams of diazotized 3-amino-6-chloroindazole. After being passed through the air for 30 seconds and through a bath at 80°C. containing, per litre of water, 1 gram of disodium phosphate, the material is rinsed, and after-treated for 20 minutes at 90°C. to 95°C. at a goods-to-liquor ratio of 1:20 in a bath containing, per litre of water, 1 gram of a reaction product from about 10 mols of ethylene oxide with 1 mol of isododecyl-phenol, 3 grams of sodium carbonate, 0.8 gram of cobalt chloride, 1.6 grams of aminoacetic acid and 0.08 gram of sodium perborate. The material is then rinsed and dried. A green dyeing having good properties of fastness is obtained.

In order to produce a white discharge, the cotton fabric is dried, after development with the diazo solution, and is then printed with a printing paste containing, per kilogram, 200 grams of sodium formaldehyde-sulphoxylate, 50 grams of the sodium salt of benzyl-sulphanilic acid (1:1), 30 grams of potassium carbonate, 30 grams of anthraquinone paste of 30% strength, 450 grams of a starch-tragacanth thickening, 100 grams of zinc white (1:1) and 140 grams of water.

The fabric is then dried, steamed, rinsed first at 90°C. with a solution containing, per litre, of water, 2.2 grams of caustic soda and then with hot water, and then after-treated as described above. A white discharge on a green ground is obtained.

By using a printing paste containing a vat dyestuff, there is produced coloured discharge on a green ground.

By using in this Example 0.8 gram of nickel sulphate, instead of 0.8 gram of cobalt chloride, there is obtained a dark violet dyeing or a white discharge on a dark violet ground.

EXAMPLE 2

A cotton fabric is dyed in the usual manner with 6.3 grams of 1-(2¹:3¹-hydroxynaphthoylamino)-2:4-dimethoxy-5-chlorobenzene and 4.48 grams of diazotized 3-amino-6-chloroindazole, per kilogram of fabric, and treated with a solution containing, per litre of water, 1.5 grams of a reaction product of about 6 mols of ethylene oxide with 1 mol of isododecyl-phenol, 7.8 grams of cobalt chloride, 8.75 grams of the sodium salt of nitrilotriacetic acid (added in the form of an aqueous solution of 25% strength), and 32 grams of the sodium salt of trichloroacetic acid, the solution being adjusted to a pH value of 6.8 by means of 6 grams of trichloroacetic acid.

The cotton fabric is then dried, and printed with a printing paste containing, per kilogram, 200 grams of sodium formaldehyde-sulphoxylate, 100 grams of zinc white (1:1), 50 grams of the sodium salt of benzyl-sulphanilic acid, 30 grams of potassium carbonate, 30 grams of anthraquinone paste of 30% strength, 450 grams of a starch-tragacanth thickening and 140 grams of water.

The fabric is then dried, steamed for 7 minutes at about 102°C., rinsed first and 90°C. with a solution containing, per litre of water, 2.2 grams of caustic soda, and then several times in the hot and in the cold, soaped with a solution containing, per litre of water, 1 gram of a reaction product of about 6 mols of ethylene oxide with 1 mol of isododecyl phenol, 3 grams of sodium carbonate and 0.5 gram of the sodium salt of nitrilotriacetic acid, rinsed and dried.

A green dyeing having white discharge effects is obtained.

EXAMPLE 3

A cotton fabric is dyed in the usual manner with 6.45 grams of 1-(6'-methoxy-2'-3'-hydroxynaphthoylamino)-2-methoxybenzene and 4.48 grams of diazotized 3-amino-6-chloroindazole, per kilogram of goods, and treated with a solution containing, per litre of water, 8.3 grams of copper sulphate, 9 grams of the sodium salt of nitrilotriacetic acid, 32.5 grams of the sodium salt of trichloroacetic acid and 1.5 grams of a reaction product from about 6 mols of ethylene oxide with 1 mol of isododecyl-phenol, the solution being neutralized with 6 grams of trichloroacetic acid.

The material is then dried, steamed for 10 minutes at about 102°C., soaped at the boil, rinsed and dried. A blue grey dyeing is obtained.

EXAMPLE 4

A cotton fabric is dyed in the usual manner with 7.5 grams of 1-(2':3'-hydroxynaphthoylamino)-2:4-dimethoxy-5-chlorobenzene and 4.1 grams of diazotized 3-amino-6-chloroindazole, per kilogram of goods, and slop-padded with a cold solution containing, per litre of water, 7.2 grams of cobalt chloride, 19.4 grams of aminoacetic acid, 50 grams of urea, 8 grams of a reaction product from 6 moles of ethylene oxide and 1 mol of isododecyl phenol and 17 cc of sodium hydroxide solution of 38° Be, and having a pH of 9.6.

The material is then dried and steamed for 7 minutes at 102°C. It is then rinsed, soaped at the boil and dried.

A green dyeing is obtained.

EXAMPLE 5

A cotton fabric, which has been dyed with the use of the diazo- and coupling components mentioned in Example 4, is slop-padded with a cold solution containing, per litre of water, 7.5 grams of copper sulphate, 22.5 grams of triethanolamine, 8 grams of a reaction product from 6 mols of ethylene oxide and 1 mol of isododecyl phenol and 50 grams of urea, and having a pH value of 8.6.

The material is dried, steamed for 7 to 10 minutes at 102°C., rinsed and soaped at the boil. A blue-grey dyeing is obtained. Instead of 22.5 grams of triethanolamine, there may be used in this Example, 38 grams of an alkaline solution of 25% strength of the sodium salt of nitrilotriacetic acid having a pH value of 11.5.

In the following Table are given further examples of components which can be used in the process of the invention, and the tints of the metalliferous azo-dye-stuffs produced on the fibre.

Diazo-Component	Coupling component	Dispersing agent	Metal salt	Complex-forming compound	Tint
2-(2 ¹ -amino-4 ¹ -methoxy-5 ¹ -methyl-phenyl)-benz-triazole-1-oxide	2:3-hydroxynaphthoyl-aminobenzene	reaction product of 10 mols of ethylene oxide with 1 mol non-ylphenol	copper sulphate	triethanolamine	dark brown
3-amino-5-chlor-indazole	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-4-chlorobenzene	"	"	"	dark blue
3-amino-6-chlor-indazole	1-(2 ¹ -hydroxyanthracene-3 ¹ -carboyl-amino)-2-methyl-benzene	"	"	"	green
"	1-(2 ¹ -hydroxyanthracene-3 ¹ -carboyl-amino)-2-methyl-benzene	"	cobalt chloride	nitrotriacetic acid	green
"	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-2-methoxybenzene	"	"	sodium polyphosphate	green
"	1-(2 ¹ -hydroxycarbazole-3 ¹ -carboyl-amino)-4-chlorobenzene	"	"	sodium pyrophosphate	grey
"	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-2-ethoxybenzene	"	"	citric acid	green

Diazo-Component	Coupling component	Dispersing agent	Metal salt	Complex-forming compound	Tint
3-amino-6-chlor-indazole	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2-methoxy-benzene	reaction product of 10 mols of ethylene oxide with 1 mol non-ylphenol	copper sulphate	oxalic acid	blue grey
"	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2-methyl-benzene	"	"	amino-acetic acid	blue grey
"	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2-methyl-benzene	"	cobalt chloride	gluconic acid	blue grey
"	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2:4-dimethoxy-5-chloro-benzene	reaction product of 6 mols ethylene oxide and 1 mol nonyl phenol	Copper sulphate	sodium pyro-phosphate	blue grey
3-amino-1-methyl-6-chlor-indazole	1-(6 ¹ -methoxy-2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2-methoxy-benzene	"	nickel sulphate	amino-acetic acid	dark blue
3-amino-1-methyl-5-nitro-indazole	2-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-naphthalene	"	"	"	dark blue
1-amino-carbazole	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2:4-dimethoxy-5-chloro-benzene	"	cobalt chloride	"	black

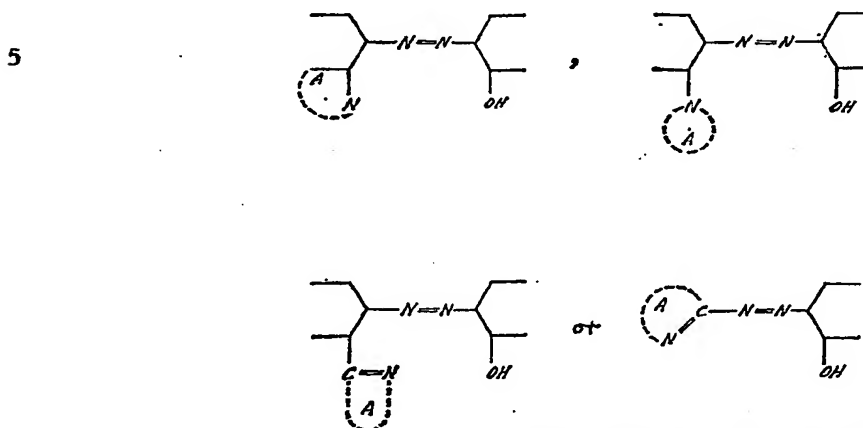
Diazo-Component	Coupling component	Dispersing agent	Metal salt	Complex-forming compound	Tint
1-amino carbazole	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2,4-di-methoxy-5-chloro-benzene	reaction product of 6 mols ethylene oxide and 1 mol nonyl phenol	copper sulphate	trietha-nolamine	blue black
7-amino-2,5-di-methyl-benzimid-azole	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2-methyl-4-chloro-benzene	"	nickel sulphate	amino-acetic acid	claret
7-amino-5-methyl-benztri-azole	2-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-3-methoxy-diphenylene oxide	"	copper sulphate	trietha-nolamine	currant
8-amino-quinoline	2:3-hydroxy-naphthoyl-amino-benzene	"	"	"	claret
"	" "	reaction product of 20 mols ethylene oxide and 1 mol octa-decyl alcohol	cobalt chloride	amino-acetic acid	garnet
"	" "	reaction product of 20 mols ethylene oxide and 1 mol oleyl alcohol	nickel sulphate	"	claret
2-(2 ¹ -amino-4 ¹ -methoxy-5 ¹ -methyl-phenyl)-benztriazole 1-oxide	2-(2 ¹ :3 ¹ -hydroxy-naphthoyl-amino)-naphthalene	reaction product of 10 mols ethylene oxide and 1 mol nonyl-phenol	copper sulphate	tartaric acid	dark brown

Diazo-Component	Coupling component	Dispersing agent	Metal salt	Complex-forming compound	Tint
2-(2 ¹ -amino-4 ¹ :5 ¹ -diethoxyphenyl)-6-methoxybenzotriazole-1-oxide	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-4-chlorobenzene	reaction product of 10 mols ethylene oxide and 1 mol nonylphenol	copper nitrate	diethanolamine	dark brown
"	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-3-nitrobenzene	reaction product of 6 mols ethylene oxide and 1 mol nonylphenol	copper sulphate	tartaric acid	dark brown
2-(2 ¹ -amino-4 ¹ :5 ¹ -diethoxyphenyl)-6-methoxybenzotriazole-1-oxide	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-4-chlorobenzene	"	copper nitrate	diethanolamine	dark brown
"	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-3-nitrobenzene	reaction product of 6 mols ethylene oxide and 1 mol nonylphenol	copper acetate	triethanolamine	dark brown
2-(2 ¹ -amino-4 ¹ :5 ¹ -diethoxyphenyl)-6-methoxybenzotriazole	2-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-naphthalene	"	"	"	dark brown
1-methyl-5-(2 ¹ -amino-5 ¹ -chlorophenyl)-1:2:3:4-tetrazole	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-2-methoxybenzene	reaction product of 20 mols ethylene oxide and 1 mol oleyl alcohol	cobalt sulphate	nitrilotriacetic acid	yellow brown
1-methyl-5-(2 ¹ -amino-5 ¹ -chlorophenyl)-1:2:3:4-tetrazole	1-(2 ¹ :3 ¹ -hydroxynaphthoylamino)-2-methyl-4-methoxybenzene	reaction product of 10 mols ethylene oxide and 1 mol nonylphenol	nickel sulphate	amino acetic acid	red brown

Diazo-Component	Coupling component	Dispersing agent	Metal salt	Complex-forming compound	Tint
2-(2 ¹ -amino-4 ¹ -chloro-phenyl)-1:5-diphenyl-1:3:4-triazole	2:3-hydroxy-naphthoyl-amino-benzene	reaction product of 12 mols ethylene oxide and 1 mol dodecylphenol	nickel sulphate	amino acetic acid	garnet
2-(2 ¹ -amino-5 ¹ -chloro-phenyl)-5-phenyl-1.3.4-oxdiazole	1-(2 ¹ :3 ¹ -hydroxy naphtho-ylamino)-2.4-dimethoxy-5-chloro-benzene	reaction product of 40 mols ethylene oxide and 1 mol castor oil	cobalt chloride	nitro-triacetic acid	red brown
2-(2 ¹ -amino-phenyl)-1:5-dimethyl-benzimidazole	1-(2 ¹ :3 ¹ -hydroxy-naphthoyl amino)-2:5-dimethoxy-4-chloro-benzene	reaction product of 6 mols ethylene oxide and 1 mol isododecyl-phenol	copper sulphate	trietha-nolamine	brown
"	1-(2 ¹ :3 ¹ -hydroxy-naphtho-ylamino)-2:4-di-methoxy-5-chloro-benzene	reaction product of 9 mols ethylene oxide and 1 mol hexyl-heptyl-β-naphthol	nickel sulphate	amino-acetic acid	garnet
2-(2 ¹ -amino-phenyl)-5-chloro-benzthiazole	1-(2 ¹ :3 ¹ -hydroxy-naphthoyl-amino)-2-methyl-4-methoxybenzene	reaction product of 10 mols ethylene oxide and 1 mol nonyl-phenol	copper sulphate	trietha-nolamine	rust red

WHAT WE CLAIM IS:—

1. A process for the production of dyeings or prints of metalliferous water-insoluble azo-dyestuffs on textile fibrous material, wherein the material is dyed or printed with a water-insoluble azo-dyestuff containing a grouping of the formula



in which A represents a 5- or 6-membered heterocyclic ring, by producing the dyestuff by coupling on the material, and the dyed or printed material is after-treated in an aqueous bath at a raised temperature with a salt of copper, nickel or cobalt, a compound capable of forming a metal complex with copper, cobalt or nickel and a detergent or a dispersing agent.

2. A process as claimed in Claim 1, wherein a water-soluble copper, cobalt or nickel salt of an inorganic acid, of a lower molecular aliphatic carboxylic acid or of an organic sulphonic acid is used as the salt of copper, nickel or cobalt.

3. A process as claimed in Claim 1 or 2, wherein an alkali metal phosphate, an alkanolamine, an aliphatic dicarboxylic acid, an aliphatic hydroxy-carboxylic acid or an aliphatic amino-carboxylic acid is used as the compound capable of forming a complex with copper, cobalt or nickel.

4. A process as claimed in any one of Claims 1 to 3, wherein a fatty alcohol polyglycol ether, an alkyl-phenol polyglycol ether, an alkyl-naphthol polyglycol ether, a fatty acid polyglycol ester or a fatty acid amide polyglycol ether is used as a detergent or dispersing agent.

5. A process as claimed in any one of Claims 1 to 4, wherein the after-treatment is carried out in an aqueous bath rendered alkaline with sodium carbonate.

6. A process as claimed in Claim 5, wherein the after-treatment is carried out at a temperature within the range of 80°C. to 100°C.

7. A process as claimed in any one of Claims 1 to 4, wherein the dyed or printed textile fibrous material is first after-treated in a bath which contains a salt of copper, nickel or cobalt, a compound capable of forming a metal complex with copper, nickel or cobalt, a detergent or a dispersing agent, and an agent capable of splitting off an alkali when heated, and then the material is steamed.

8. A process as claimed in any one of Claims 1—7, wherein there is used a water-insoluble azo-dyestuff defined in Claim 1 and obtainable by coupling a diazotized 2 - (2¹ - aminoaryl) - 4:5 - arylene - 1:2:3 - triazole or -1:2:3 - triazole - 1-oxide, 1- or 5 - (2¹-aminoaryl) - 1:2:3:4 - tetrazole, 2 - (2¹ - aminoaryl) - 1:3:4 - triazole, -1:3:4 - oxadiazole or -1:3:4-thiodiazole, 8-aminoquinoline, 3- or 7-amino-indazole, 7-amino-benzimidazole or -benztriazole, 1-aminocarbazole, 2 - (2¹ - amino-phenyl) - benzimidazole or -benzthiazole, 4-aminobenzo-2:1:3-thiodiazole or 3-amino-1 - phenyl - 5 - imino - 4:5 - dihydro - 1:2:4 - triazole with an arylide of an aromatic or heterocyclic ortho-hydroxy-carboxylic acid, an acyl-acetic acid arylide or other aromatic or heterocyclic hydroxy-compound or compound containing an enolised or enolisable keto-methylene group in a heterocyclic ring and capable of coupling in a position vicinal to a hydroxyl group.

9. A process for the production of a dyeing or print of a metalliferous water-insoluble azo-dyestuff on a textile fibrous material conducted substantially as described in any one of the Examples or with reference to the Table herein.

10. Textile fibrous materials, which have been dyed or printed by the process claimed in any one of Claims 1—9.

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court, Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press
(Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings,
London, W.C.2, from which copies may be obtained.